The Maturity Estimation of Material Organic in CaCO₃ with Determining $T_{\text{max}}$ and Energy Activation Using Pyrolysis Method

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Shale material is shale oil that is clay or carbonate material contain excessively immature organic. When heated to a certain temperature, the organic content changed to mature and changed in physics and chemistry, so it can produce energy materials such as oil and gas. The testing of TOC that produced carbonates-organic showed excellent quality as shale oil (TOC ≥ 12.0%). The results of thermogravimetric analysis showed activation energy of carbonates was 749–1339 kJ/mol and the temperature of the reaction process was 75–740 °C. Organic composition that was larger than carbonate can caused a smaller activation energy. The carbonate content of OD7-Asl2 had $E_a = 1083.7$ kJ/mol smaller than OD7-Asl1 with $E_a = 1338.1$ kJ/mol. A very large TOC value affected the activation energy to be smaller, as the carbonate of OD7-Asl2 was smaller than OD7-Asl1. The maturity of the OD7-Asl2 shale occurred at $T = (380–445)$ °C, $E_a = 1083.7$ kJ/mol and $T_{\text{max}} = 415$ °C, better than OD7-Asl1. The Rock Eval Pyrolysis test results showed shale carbonate had a high potential to produce oil and gas. Shale material heating result reinforced by FTIR testing that the compounds with specific functional groups apart and a new peak appeared at wavenumber 2900 cm$^{-1}$ which indicate the presence of hydrocarbons single bonds.

Keywords: Oil Shale, TOC, Activation Energy, Pyrolysis.

1. INTRODUCTION

Oil shale is a kind of clay or carbonate material that contains a lot of organic materials, and an energy source that can produce oil and gas [10] (Kantsler and Cook, 1980). The result of oil shale processing is very useful in the agricultural sector and property industry [1–3]. A research on the oil shale becomes a main research in Soviet Union [21]. Berraja et al. [5] started the research on thermal analysis study at the combustion of oil shale in Tafaya.

From the results of research by Mulyanto et al. [26]: Organic substances that are in sedimentary rocks or carbonate will undergo chemical and physical changes, caused by temperature, heat, pressure and age. Such changes can lead to the formation of oil or gas. To predict the properties of rock containing organic matter, inquiry can be done by looking the chemical and physical properties. To determine the chemical and physical properties, can be used petrophysical and geochemical technology, supported by geological data, seismic technology and technology geothermal (heat).

The Rock-Eval Pyrolysis method has been initiated by Katz [19] to analyze the organic material. Bartis et al. [4] did the oil shale exploitation that was gathered and sent to the processing place by burning the oil shale to be utilized as a source of electrical energy. Then Burnham et al. [6] did the extraction on the result of shale material processing which was done on the ground (ex-situ processing), and there were some new technologies which carried out the extraction on the shale material underground (in situ processing).

The processing of carbonate or clay shale material has not been done in Indonesia, but the reserve of shale material in Indonesia has been mapped. Geological Resource Centre has conducted the research on the oil shale material in 53 locations in Indonesia. The processing of shale material by heating requires some appropriate parameters, so that the changing reaction (maturation) in physics, chemistry and biology can occur in accordance with the desire. Some of the parameters associated with the variation or organic maturity level is the temperature, the energy activation (inversely proportional to the velocity of the reaction) and the material type. In this case, the maturation is defined as maturation of the organic material in the
carbonate material, or often referred to shale material or oil shale.

From the results of Dewanto et al. [11] research: The time to change the immature organic clay and organic carbonate material into oil and gas (energy source), is determined by the characteristics of the shale material, which are: the immature hydrocarbon substance has API gravity and boiling point which is close to petroleum’s boiling point; the heating process at temperature of 200 °C to 400 °C changes the substance into shale material with low boiling point; this is due to the high degree of its API so it contains more light fractions such as gasoline, thus its boiling point is low.

In this research, the production of carbonate shale material is by compounding the organic material and CaCO₃. The compounding is done using the way of weight percentage ratio variation, mixing, mixing time and the last is the result of TOC testing (pyrolysis), where the value of TOC is ≥12.0% [32] as a requirement of good oil shale material. The material mixture is modified by the ratio of: organic = calcite and organic > calcite. The TOC testing that produces carbonate shale material shows an excellent quality of oil shale (TOC ≥ 12.0%), which is confirmed by the result of SEM analysis (morphology and composition) and XRD (the interaction of two materials). By determining the level of organic maturation in CaCO₃, then the task will be more structured and accurate. Reaction stage-1 is immature, which is the immature organic material; reaction stage-2 is mature-1, which is the mature organic material or starting to crack material; reaction stage-3 is mature-2 and over mature-1, which is the organic material turning into hydrocarbon and some generating the gas; reaction stage-4 the release of all gases.

The reaction stages are closely related to the energy activation (including temperature and reaction velocity), and the type of shale material (carbonate-organic). By knowing the parameter value (from the result of the energy activation) and the type of material, then the shale material processing in term of temperature setting can be determined, so that no error occurs in the heating process.

The Rock-Eval Pyrolysis testing is not only used to determine the total organic carbon (TOC), but also to determine the value of $T_{\text{max}}$ (maximum temperature). Then to determine the maturity of organic material, detect oil and gas reserve and to reidentify the type of some material mixture.

The TGA testing is conducted to determine the value of the energy activation. By conducting a series of tests to obtain a pair of $dY/dt$ and $T_{\text{solid}}$, so the chart of $\ln(dY/dt)$ with $1/T_{\text{solid}}$ can be made. Then the straight-line equation of the chart is searched by using linear regression, so the value of the energy activation can be determined from: $E = -aR$, the value of pre-exponential factor ($A$) is found when the chart of $y = ax + c$ intersects the y axis or $1/T_{\text{solid}} = 0$ [7, 15, 31].

The formulation and analysis on the energy activation is based on some previous researchers, namely: Pogaku et al. [27] conducted a research on the energy activation and the velocity enzyme-catalyzed reaction. There are several researchers conducting research on the activation of SiO₂ energy which depends on the input power. Indrati et al. [15] conducted a research on the energy activation of pellet (Th, U)O₂ at the stage of pellet growth using a dilatometer and Scanning Electron Microscope (SEM). Cahyadi et al. [7] conducted a research on the behavior of Indonesia’s coal particle ignition using Thermogravimetric Analysis at the condition of O₂/N₂ and O₂/CO₂. Sato et al. [28] conducted a research on the activation free energy that has a dependence on the temperature. The temperature dependence is found greater for the calculation. The determination of the energy activation, pre-exponential factor and reaction velocity from TGA analysis refers to several researchers, they are: Katarzyna et al. [18], Himawanto [13], Himawanto et al. [14], Emam [12], Marnoto [23], Yan and Zhang [33], Sugondo [29], Sukma [30], Malika et al. [22], Martono et al. [24], Cantrell et al. [8], Suyitno [31], Kholisoh [20], Minarsih [25], Jiang et al. [16].

Through this research, it is expected that the shale material (Carbonate-Organic) which has been characterized by a variety of methods, can be obtained its physics and chemistry property information to understand the detail of mechanism and the active site on both shale materials, then compare and determine the best one, so that the parameter of laboratorium test can be determined for making the conversion model on the reaction of shale material into crude oil. Further, it is hoped that it can be used as the raw material of the oil shale processing, as the raw material which is excessively available in Indonesia and ready to be used as one of the alternative energy resources.

2. METHOD OF RESEARCH

The Selection of Carbonate and Organic

The stage of determining material type is the most important stage in the material selection. Firstly, choose the material from the result of coring drilling, then the material is grouped, namely the carbonate material group type calcite (CaCO₃). The carbonate material must be completely clean from fluid and natural hydrocarbon, therefore prior to the measurement of porosity and permeability, the material should be in dry condition (dry sample). Secondly, determine the material organic cyclic group, namely salicylic acid (C₆H₅O₃).

The Characterization of Carbonate and Organic

The tools used for the characterization of clay and carbonate are SEM and XRD, in order to know the identity of the material. SEM is used to know the type of elements, distribution, topography and the surface shape. The XRD
The technique can show the type and compound percentage as well as the characteristic of the crystallography.

**The Making of Shale Material (Carbonate-Organic) and TOC Testing**

The forming method of carbonate shale material is by stirring for a long time, then pressing slowly and leaving to stand for a moment (72 hours) and stirring again and also pressing slowly again, the purpose is to make the organic material fills all pores of the carbonate material. Furthermore, the shale material is left to stand at least 48 hours, the purpose is to make the trapped organic material (fills) the pores and be more binding and cohesive. Then the TOC is tested and made like an oil shale, with the same number (2, 72); $E$: The energy activation (J/mol) or $E_a$; $R$: The gas constant (8, 31 J/mol °K); $T$: The material temperature (°K).

$x$ is the mass fraction, which is calculated by the formula of,

$$x = \frac{m_0 - m}{m_0 - m_f}$$  \hspace{1cm} (2)

where $m$ is the mass of the sample when the time is $kt$, $m_0$ is the initial mass of the sample and $m_f$ is the final mass of the sample. The heating rate is defined,

$$\beta = \frac{dT}{dt}$$  \hspace{1cm} (3)

By combining the Eqs. (1)–(3), so the Eq. (1) becomes,

$$\frac{dx}{dt} = \frac{A}{\beta} e^{-E_a/RT} (1 - x)$$  \hspace{1cm} (4)

$$\frac{dx}{(1 - x)} = \frac{A}{\beta} e^{-E_a/RT} dT$$  \hspace{1cm} (5)

If both sides are integrated, so the Eq. (5) will be,

$$-\ln(1 - x) = \frac{A}{\beta} \int e^{-E_a/RT} dT$$  \hspace{1cm} (6)

In the Eq. (6), the term $\int e^{-E_a/RT} dT$, is an inexact integral but it can be expressed in the asymptotic series, so that the Eq. (6) can be integrated to be,

$$-\ln(1 - x) = \frac{AR^2}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) e^{-E_a/RT}$$  \hspace{1cm} (7)

$$-\ln \left( \frac{1 - x}{T^2} \right) = \frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) e^{-E_a/RT}$$  \hspace{1cm} (8)

$$\ln \left[ -\frac{\ln(1 - x)}{T^2} \right] = \ln \left[ \frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{RT}$$  \hspace{1cm} (9)

In the fact, the term of:

$$\frac{2RT}{E_a} \ll 1$$

So it can be ignored and the equation becomes,

$$\ln \left[ -\frac{\ln(1 - x)}{T^2} \right] = \ln \left( \frac{AR}{\beta E_a} \right) - \frac{E_a}{RT}$$  \hspace{1cm} (10)

By making the connection chart between $\ln[-\ln(1 - x)/T^2]$ and $1/T$, the straight line can be obtained where the slope of the line is $-E_a/R$, so that the value obtained is $E_a$. The delineation chart of the relationship between $\ln[-\ln(1 - x)/T^2]$ and $1/T$ heating process as a basis for calculating the energy activation on the shale material heating.
**Determining the Maximum Temperature ($T_{\text{max}}$) by Pyrolysis Testing**

$T_{\text{max}}$ is the maximum temperature to release the hydrocarbon from the cracking process of the material mixture that occurs during the pyrolysis. $T_{\text{max}}$ is an indication of organic maturation stage in the shale-carbonate. The $T_{\text{max}}$ value is one of the geochemical parameters used to determine the maturity level of shale-carbonate. The value $T_{\text{max}}$ that recorded is influenced by several types of material mixtures mentioned above. Some of the material mixtures will form the different hydrocarbons at the same temperature condition. The $T_{\text{max}}$ value as an indicator of maturity also has some limitations such as it can not be used for some types of materials that have low TOC.

**3. RESULTS AND DISCUSSION**

Figure 1 shows the description of determination of material type to the processing step in the laboratorium, starting from the coring process, the material selection, the production of carbonate-organic material sample, and also the tests.

**The Selection of Carbonate and Organic**

The carbonate material that has been formed as pellet with a variety of diameter sizes is shown at Figure 2, where the material is already in dry condition.

Some of carbonate materials used is the material with the sample number OD7, while the organic material chosen is group of cyclic compound such as salicylic acid.

**The Determination of TOC (Total Organic Carbon) and $T_{\text{max}}$ on Carbonate Shale Material**

The result of shale material manufacture (CaCO$_3$–C$_7$H$_6$O$_3$) shows a very good result as oil shale, because it has a value of TOC $\geq 12\%$ and the characteristic is the same as oil shale. The TOC testing is successfully performed on the sample of carbonate-organic material (OD7-Asl). This TOC value is used as one of the parameters for initial selection stage on the material selection in order that can be used as shale material (oil shale), so that the bad and good material can be separated to be the raw material of further processing.

The carbonate-organic shale material has shown the excellent quality, which has a value of TOC $\geq 12.0\%$. Table I shows the value of TOC and $T_{\text{max}}$ from the result of pyrolysis that is used as an initial indicator of the thermal maturity level of carbonate-organic shale material. The material maturity shows a varied value, and the carbonate shale of OD7-Asl1 requires a greater temperature than the carbonate shale of OD7-Asl2. The combination between TOC and $T_{\text{max}}$ indicates that the carbonate shale material that acts as oil shale is likely more potential as oil and gas.

**The SEM Analysis on the Organic Material**

Figure 3 shows the SEM image and Edax on the salicylic acid (C$_7$H$_6$O$_3$) organic material.

From the result of Edax, the organic material has a dominant content of C and O. The organic material infiltrates into the Kerogen type II which can be formed from some different sources, namely the marine algae, pollen and spore, wax layer of plant, resin fossil, beside that it also derives from the plan fat. This occurs due to the mixing
of organic material *autochton* with *allochton* material that dominated by material from plants such as pollen and spore. Its SEM image looks like the bonded white blobs.

**The SEM Analysis on the Carbonate Material**

Figure 4 shows the result of SEM analysis on the carbonate material (OD7). The carbonate material (OD7) has many pores. Some areas of the pore cavity can be filled with other material (C–E, 2–4). The carbonate material is dominated by calcite (D–E, 2–3; B–D, 2–4) and a little dolomite (C–D, 5–6). Besides the carbonate material is dominated by the carbonate, it also has little clay material (illite dan kaolinite) that is situated around the pores. The type of the pore is secondary pore, where the distribution of the secondary pore is caused by the dissolution of planktonic (C–D, 2). From the result of Edax SEM on the carbonate CaCO₃, it has a great content of Ca and O (dominant).

**The SEM Analysis on the Carbonate Shale Material (Carbonate-Organic)**

The surface area of the shale material that has been filled by the organic is smaller, so it can be indicated that the place of the carbonate has been filled by the organic, because the pores becomes smaller. The SEM image of the carbonate shale (calcite) has the dominant secondary pores. At a certain time, the porosity will change and cause the organic material exits and enters the pores. The calcite material is success as a place of perfect maturation of organic material.

Figure 5 shows the carbonate shale material OD7-Asl2 (33% CaCO₃ and 67% salicylic acid). From the result of Edax SEM on the carbonate shale OD7-Asl2, it contains some elements with (wt, %) dominated by Ca, O and C, as follows Carbon (43.65%), Oxygen (40.81%) and Calcium (11.78%).

**The Measurement of X-ray Diffraction (XRD)**

The result of the carbonate OD7 characterization is in the form of diffraction patterns which are the peaks characteristic of crystal CaCO₃ structure. Figure 6 shows the chart of the XRD result on the shale material (carbonate-organic) OD7, OD7-Asl1, OD7-Asl2, and OD7-Asl3. The diffraction patterns of CaCO₃ are identified at the angle of 2θ. If the peaks of CaCO₃ characteristic appear, so the compound phase can be identified. The X-ray diffraction pattern that formed is the result of atoms scattering that is located on the *hkl* plane in the crystal. The carbonate OD7 has five high peaks and the intensity will change when there is an organic addition. The angle 2θ position is at the angle of 26.6°, 29.4°, 36.0°, 39.5° and 43.3° with the intensity values captured by the X-ray detector are 779 cts,

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**Table I.** The result of TOC (total organic carbon) testing.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample name</th>
<th>TOC (%)</th>
<th><em>T</em>&lt;sub&gt;max&lt;/sub&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>OD7-Asl1 (50% CaCO₃ + 50% C₇H₆O₃)</td>
<td>12.01</td>
<td>432</td>
</tr>
<tr>
<td>2.</td>
<td>OD7-Asl2 (33% CaCO₃ + 67% C₇H₆O₃)</td>
<td>12.89</td>
<td>415</td>
</tr>
<tr>
<td>3.</td>
<td>OD7-Asl3 (67% CaCO₃ + 33% C₇H₆O₃)</td>
<td>9.14</td>
<td>493</td>
</tr>
</tbody>
</table>
The carbonate shale material OD7-Asl1 has five highest peaks at the same angle position of 2θ as the shale material OD7-Asl2, which are at the angle of 10.94°, 17.21°, 25.23°, 28.70° and 29.41°, with the intensity values captured by the X-ray detector are 47282, 44513, 18466, 8361 and 12199 cts. The peaks that formed are the peak of crystal Carbon Dioxide, Fichtelite C_{19}H_{34}, Calcium, Carbon and Calcite CaCO_3, and it can be identified that the crystal planes or Miller indices hkl are (100), (200), (110), (231) and (104). The shale material (carbonate-organic) OD7-Asl3 has 5 highest peaks at the position of 2θ, which are 10.96°, 17.23°, 25.24°, 26.61° and 29.43°, with the intensity values captured by the X-ray detector are 12771, 13314, 4687 and 18095. From the result, it can be concluded that the peaks that formed are the peak of crystal Fullerite, Nitrammite N_2H_4O_3 and Calcite CaCO_3, and it can be identified that the crystal planes or Miller indices hkl are (111), (101), (002), (003) and (104). The addition of organic material (C_{7}H_{6}O_{3}) is performed on the natural carbonate (OD7) with a particular composition. At the angle of 2θ = 29° with the same hkl plane, the calcite (104) condition experienced on the shale material is the intensity of OD7 ≥ OD7-Asl3 > OD7-Asl1 > OD7-Asl2. While at the angle of 2θ = 25° and the angle of 2θ = 17°, the condition experienced on the carbonate material is the intensity of OD7 ≤ OD7-Asl3 < OD7-Asl1 < OD7-Asl2. The result of XRD characterization on the carbonate shale material which has the highest intensity is shown in the Table II.
Fig. 6. The XRD characterization on the carbonate and shale material (carbonate-organic).
Table II. The XRD characterization on the carbonate shale material which has the highest intensity.

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>OD7</td>
<td>29.48</td>
<td>20383</td>
<td>3.03</td>
<td>104</td>
<td>Calcite, CaCO3</td>
</tr>
<tr>
<td>2.</td>
<td>OD7-Asl1</td>
<td>10.94</td>
<td>46314</td>
<td>8.08</td>
<td>100</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>3.</td>
<td>OD7-Asl2</td>
<td>10.94</td>
<td>47282</td>
<td>8.08</td>
<td>100</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>4.</td>
<td>OD7-Asl3</td>
<td>29.43</td>
<td>18095</td>
<td>3.03</td>
<td>104</td>
<td>Calcite, CaCO3</td>
</tr>
</tbody>
</table>

Fig. 7. The chart of thermogravimetry (TGA) analysis result on the shale material (OD7-Asl1).

Fig. 8. The chart of thermogravimetry (TGA) analysis result on the shale material (OD7-Asl2).

The detector on every sample, has different value. High or low the X-ray intensity that captured by the X-ray detector is influenced by the level of the regularity of atom formation in the crystal that is diffracted by X-ray. The more atoms are structured regularly, the higher the intensity that captured by the detector. When the intensity is greater means the sample has the greater crystal regularity or more well arranged atoms in the layers. The X-ray diffraction patterns that formed are the result of atoms scattering that located at the hkl plane in the crystal. Any difference or change in the compound and hkl plane at the same angle of 2 theta at every organic addition, it means the reaction occurs between CaCO3 material and organic.

The Result of TGA Testing on the Shale Material (Carbonate-Organic)
The test is carried out on the carbonate shale material OD7-Asl1, with the composition of 50% CaCO3 and 50% C7H6O3. The result of TGA testing on the shale material OD7-Asl1 is shown on Figure 7. The first change occurs at the temperature of 75 °C–170 °C, this is where the loss of water molecules happens in the crystal structure. At the temperature of 225 °C–275 °C, the second weight change that significant occurs, and it is indicated as the change in the structure on the carbonate shale material and the loss of water molecules chemically.

When the calcination is reperformed, the weight loss occurs at the temperature of 325 °C–450 °C, then the molecules in the carbonate shale are released, so that it will affect the change on the pore size. The interval temperature of 325 °C–450 °C indicates the maximum temperature that required for carbonate shale to turn into oil. The last change phase occurs at the temperature about 650 °C–740 °C. This condition can be called as over mature, where the chart line has shown a tendency of straight horizontal. Physically, the material that
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has been calcined at the temperature above 740 °C, the color becomes blackish. So the temperature that required at the process of the change (reaction) of oil shale material on the carbonate shale to be oil is about ±(325 °C–450 °C).

Then the TGA testing is performed on the material OD7-Asl2 (calcite-salicylate), namely the test on the carbonate shale material where the composition is the mixture of 33% CaCO₃ and 67% C₇H₆O₃. This test is performed to know the structural damage when heating at the high temperature is carried out (over 400 °C), because it can provide the description of the change process in the substance mass. The result of TGA testing on the shale material OD7-Asl2 is shown on the Figure 8.

The first weight loss occurs at the temperature of ±95 °C–205 °C, it indicates the water molecules apart from the crystal structure of OD7-Asl2. Then the second weight loss occurs at the temperature around 225 °C–285 °C. The second significant weight change indicates the change in the structure of the material OD7-Asl2 and the loss of water molecules chemically. Then the third weight loss occurs at the temperature of 380 °C–445 °C, where the molecules in OD7-Asl2 is apart. The interval of temperature indicates the maximum temperature that required by OD7-Asl2 (carbonate shale) to begin turning into oil. When the calcination is always performed to the last loss until becoming constant, which is at the temperature of 610 °C–720 °C, then many molecules in OD7-Asl2 (the carbonate shale) are apart, so that there is part of the shale in the pores is also apart. This condition can be called as over mature, where the line of the chart shows a tendency of straight horizontal along with the increasing of the temperature up to 720 °C. Physically, the material that has been calcined at the temperature above 720 °C, the color becomes blackish. So the temperature required for the maturation process of the oil shale OD7-Asl2 into crude oil is about ±(380 °C–445 °C).

The Duration of Heating the Material

The carbonate shale material OD7-Asl2 undergoes the heating process faster than the material of OD7-Asl1.

Figure 9 shows the relationship between the mass loss versus the time on the carbonate shale material. The
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greater ratio of organic composition than calcite causes maturation reaction in the heating process becoming faster.

The Energy Activation and Pre Exponential Factor of Shale Material OD7-Asl1

The TGA gradual decomposition process that is used alone or combined with DTA can separate and determine each stage. On this shale material sample (carbonate-organic), the four-level decomposition occurs, it can be seen on Figure 7. The result of TGA shows that the decomposition level of shale material is divided into four levels of temperature, which are level I is between the temperature of 75 °C–170 °C, level II occurs between the temperature of 225 °C–275 °C, level III is between the temperature of 325 °C–450 °C and level IV occurs between the temperature of 670 °C–740 °C. Figure 10 shows the method of determining the energy activation \(E_a\) and the pre exponential factor of OD7-Asl1. In the process of heating the material OD7-Asl1, the decomposition goes through four stages. The TGA and DTA can be used in a variety of kinetic studies. The fast and accurate TGA method is used to study the decomposition reactions isothermally. This process can be repeated at other temperature and the result is analyzed to determine its energy activation.

The energy activation \(E_a\) values and pre exponential factor of each reaction stage at 4 levels reaction are shown in Table III.

The total value of the energy activation on the heating of the material OD7-Asl1 is \(E_a = 1338.1\) kJ/mol and the pre exponential factor is \(A = 172\).

The Energy Activation and Pre Exponential Factor of Shale Material OD7-Asl2

The gradual decomposition process on the shale material OD7-Asl2 (carbonate-organic) occurs on four levels decomposition, it is shown on the result of TGA testing on Figure 8. The decomposition level of shale material OD7-Asl2, from the result of TGA is divided into four levels of temperature, which are level I is between the temperature of 95 °C–205 °C, level II occurs between the temperature of 225 °C–285 °C, level III occurs between the temperature of 380 °C–445 °C and level IV occurs between the temperature of 610 °C–720 °C. The chart of the energy activation \(E_a\) and pre exponential factor determination of OD7-Asl2 is shown on Figure 11. The total value of the energy activation on this shale material (the organic ratio is greater) has value of \(E_a = 1083.7\) kJ/mol, and the pre exponential factor of \(A = 137.2\), where the value of \(E_a\) and \(A\) is smaller than the OD7-Asl1 material, so that the velocity of the reaction is faster. The complete energy activation \(E_a\) values and pre exponential factors for each reaction stage on 4 levels temperature are shown in Table IV.

<table>
<thead>
<tr>
<th>Reaction level</th>
<th>(E_a) (kJ/mol)</th>
<th>(A) (%/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 °C–170 °C</td>
<td>102.89</td>
<td>17</td>
</tr>
<tr>
<td>225 °C–275 °C</td>
<td>333.32</td>
<td>62</td>
</tr>
<tr>
<td>325 °C–450 °C</td>
<td>200.79</td>
<td>22</td>
</tr>
<tr>
<td>670 °C–740 °C</td>
<td>701.14</td>
<td>71</td>
</tr>
</tbody>
</table>

Table III. The \(E_a\) and \(A\) values of OD7-Asl1 material.
4. CONCLUSION

The energy activation of carbonate shale material is $E_a = 749–1339$ kJ/mol and temperature for the process of carbonate shale material reaction is $T = 75–740$ °C.

The composition ratio (wt.%) of organic that is greater than carbonate causes the carbonate shale material (with TOC ≥ 12%) having a lower energy activation. The carbonate shale material of OD7-Asl2 (33% carbonate +67% organic) has $E_a = 1083.7$ kJ/mol lower than OD7-Asl1 (50% carbonate +50% organic) that has $E_a = 1338.1$ kJ/mol.

The reaction level is higher, influences the energy activation reaction becoming smaller (see number 2), namely carbonate shale material OD7-Asl2 is smaller than OD7-Asl1.

The maturity of shale material OD7-Asl2 occurs at $T = (380–445$ °C), $E_a = 1083.7$ kJ/mol and $T_{max} = 415$ °C, it is better than OD7-Asl1 which occurs at $T = (325–450$ °C), $E_a = 1338.1$ kJ/mol and $T_{max} = 432$ °C.

References


Received: 1 January 2019. Accepted: 11 March 2019.